

# PATENT SPECIFICATION

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## (54) PHOTOGRAPHIC LIGHT-SENSITIVE MATERIALS

(71) We, FUJI PHOTO FILM CO., LTD., a Japanese Company, of No. 210, Nakanuma, Minami/Ashigara-Shi, Kanagawa, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a photographic material having improved anti-static properties and mechanical workability.

A photographic light-sensitive material is generally prepared by pre-coating a support with a subbing layer intended to improve the adhesion of a subsequently applied hydrophilic coating, and then coating a light-sensitive photographic emulsion on one or both surfaces of the subbed support. The support may be, for instance, a poly- $\alpha$ -olefin such as polyethylene or polystyrene, a cellulose ester such as cellulose triacetate, a polyester such as polyethylene terephthalate, a paper, a synthetic paper, or a paper coated on both surfaces thereof with a polymer. An example of a photographic material having photosensitive silver halide emulsion layers on both surfaces of the support is a direct X-ray (radiographic) film, but other photographic light-sensitive materials ordinarily have the photographic silver halide emulsion layer(s) on only one surface of the support, the opposite surface or "back" of the support being uncoated.

Since such a photographic material is composed of a support and one or more photographic emulsion layers which are electrically insulating, static charges tend to be formed thereon by friction or merely by contact with similar or dissimilar surfaces (such as rubber, metal, plastics or paper) during the manufacture or use of the photographic material. For instance, static charges are caused by friction of a film against rollers during the production of photographic films or by contact or separation between the surface of a support or film cartridge and the surface of a photographic emulsion layer coated on the support during the rolling or unrolling step. Static charges are also caused in cine film by friction thereof against the mechanical parts of the camera during photography or rolling up or by contact between the surface of the film base and the surface of the photographic emulsion layer. Furthermore, static charges are caused in an X-ray film by contact thereof with the mechanical parts of an automatic X-ray camera or by contact of the film with X-ray fluorescent sensitizing paper.

These static charges cause various problems. For instance, the static charges accumulated on a photographic film prior to development cause an electric discharge which has the effect of local irradiation of the photosensitive film and manifest themselves by the formation of irregular spots or lines. Those spots or lines formed by the static discharge are called "static marks", and they reduce or completely destroy the commercial value of the photographic film; for instance, the presence of static marks on medical or industrial X-ray films can be very dangerous. This phenomenon is a most troublesome problem since the formation thereof is not perceptible before development, and it is accentuated by increase in the photographic sensitivity of the material and in the speed of processing. Also, such accumulated static charges cause the adhesion of dust on the surface of support films, which results in secondary difficulties such as uneven coating of layers thereon.

It is believed that the frictional or contact charging is caused by an ionic interaction between the materials on contact, but it is difficult at present to predict, from a knowledge of the chemical structure of the material, which materials are charged positively and which negatively. However, it is obvious that the accumulation of static charges can be prevented by reducing the charge potential or by eliminating static charges in a quite short period of time before the local discharge of the accumulated

static charges, by increasing the electrical conductivity of the surface of the materials.

Attempts have been made to improve the electrical conductivity of supports and the surface of various surface layers of photographic materials by utilizing various hygroscopic materials, water-soluble inorganic salts, and certain surface-active agents.

For instance, in order to provide an antistatic property to the supports for photographic films it is known to incorporate an antistatic agent actually in the polymer used for making the supports or to coat an antistatic agent on the surfaces of such supports. In coating an antistatic agent, the antistatic agent is coated as the backing layer alone or as a mixture with a polymer such as gelatin, polyvinyl alcohol or cellulose acetate. An antistatic agent may also be incorporated in the surface protective layer for the photo-sensitive emulsion layer of a photographic material or a solution of an antistatic agent is coated on the surface layer of a photographic material.

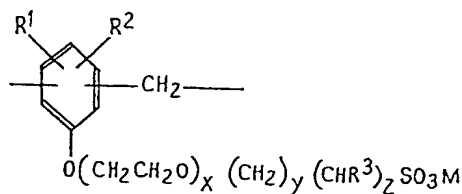
However, various conventional antistatic agents are quite specific to the nature of supports for photographic films and the nature of photographic compositions, namely, certain antistatic agents may give good results for specific film supports, photographic silver halide emulsions, and constituents for photographic films or papers but do not provide any antistatic effect to other film supports and photographic constituents and additionally sometimes adversely influence the photographic properties.

Antistatic agents ordinarily used effectively not only in photographic materials but also in various other fields are generally so-called surface-active agents, i.e., compounds which have both a hydrophobic aliphatic hydrocarbon group and a hydrophilic group such as a sulphonate group, a phosphate group, a carboxylate group or a quaternary ammonium salt group in the molecule. It is believed that among these surface-active agents, those having a substantially high power of absorption are effective for the purpose. However, when such surface-active agents are applied to photographic materials, they generally tend to smooth the surface of the photographic film as the number of carbon atoms of the hydrophobic group in the molecule increased. When the surface-active agent is used in the backing layer of the support for the photographic film this smoothing effect is most noticeable and is advantageous in reducing adhesion of the film to itself, facilitating its passage through the camera, and improving the quality of the photographic layers. Therefore, the sparingly water-soluble or water-insoluble hydrophobic compounds are known to be used for providing a slip property, apart from any antistatic property.

However, in this case, the provision of too high a slip property is accompanied by such undesirable disadvantages such as slipping and scratching of photographic films during the manufacture of the films, uneven cut sizes of photographic films on cutting, slipping on stacking, splitting or unwinding of the photographic film in a camera and flowing of images on projection. Therefore, in selecting antistatic agents for photographic materials, it is necessary to consider whether the antistatic agents adversely affect the camera behaviour of the photographic materials and the adhesive property while maintaining a suitable coefficient of friction.

An object of this invention is to provide a photographic material having an improved antistatic property and an improved mechanical workability without reduced photographic properties.

According to this invention, a photographic material comprising a support having thereon at least one silver halide light-sensitive emulsion layer and at least one other layer contains a compound consisting essentially of recurring units represented by the general formula:



(I)

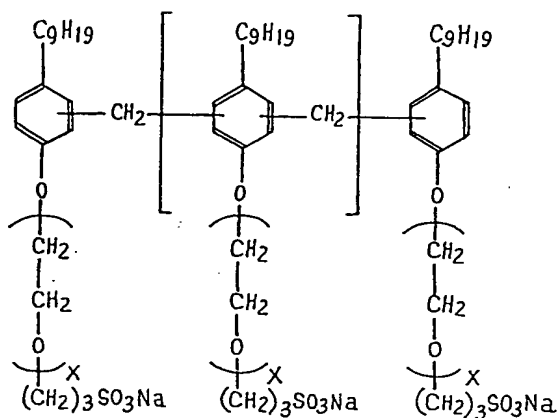
wherein R<sup>1</sup> represents a hydrogen atom or an alkyl group, R<sup>2</sup> represents an alkyl group, R<sub>3</sub> represents a hydrogen atom or a methyl group, M represents a hydrogen atom or a cation, x has a value of from 0 to 50, y represents 0, 2 or 3, and z represents 0 or 1, provided that x, y and z are not all simultaneously zero. The or each other layer may be, e.g., a surface (protective) layer, an anticurl layer or an antihalation layer. The above compound may be contained in any of the aforesaid layers or may be coated in a composition on at least one surface layer of the support.

The compound of the general formula (I) used in this invention (otherwise referred to as the "polymer" or as the "antistatic polymer") can be described as an ethylene oxide addition product of recurring units of an alkyl-substituted phenolphormaldehyde condensate wherein the mean polymerization degree of the polymer (i.e. number of repeating units) is generally 2 to 20, preferably 2 to 10. The phenyl group must be substituted by at least one alkyl group, in order to obtain the desired antistatic effects; in di-substituted groups the alkyl groups can be the same or different. There are no particular limitations on the number of carbon atoms in the alkyl group or the alkyl-substituted phenyl group; suitable alkyl groups are those containing 1 to about 18 carbon atoms, preferably 4 to 18 carbon atoms. Suitable examples of the cation M are an alkali metal, an alkaline earth metal, ammonium or a substituted ammonium salt, such as Na, K, Li, Ca, Ba,  $\text{NH}_4$ ,  $\text{HN}(\text{CH}_3)_3$  or  $\text{HN}(\text{CH}_2\text{CH}_2\text{OH})_3$ .

In the above general formula and in the specific formulae set forth below,  $x$  representing the number of ethylene oxide units present can be 0 or an integer of 1 to 50. These materials are generally obtained as a mixture of polymers of varying chain length, and  $x$  thus may have a non-integral value as an *average* number of ethylene oxide units. Polymers containing at least one ethylene oxide unit, i.e., where  $x$  is 1 to 50, show better antistatic properties than those not containing ethylene oxide units and are therefore preferred. Most preferably  $x$  has a value of 1 to 20.

The formulae of some compounds which can be used in this invention are shown below and designated Compounds 1 to 8 (by which they are later referred to in the Examples):

Compound 1.



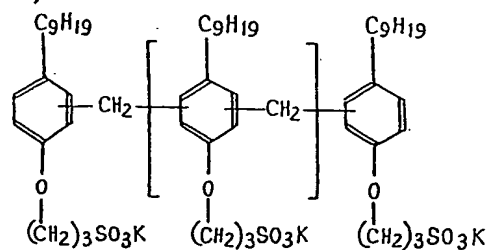
The mean polymerization degree is 3 and  $x$  is 2.5.

Compound 2

A compound having the same structure as Compound 1, but in which the mean polymerization degree is 3 and  $x$  is 10.

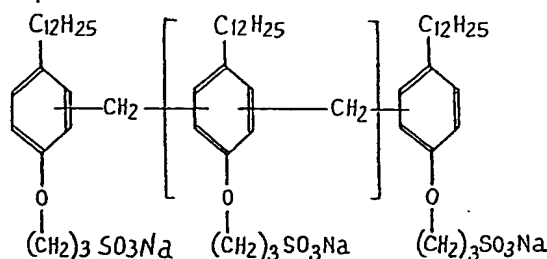
10

Compound 7



The mean polymerization degree is 5.

Compound 8



The mean polymerization degree is 7.

The polymers of the aforementioned general formula used in this invention can be prepared by various known methods. For instance, the compound can be obtained by preparing an alkylphenolformaldehyde condensate and then the ethylene oxide addition product of the condensate by the methods as described in *Kogyo Kagaku Zasshi (Journal of Industrial Chemistry)*, 66, 391 (1963) and *Yu Kagaku (Oil Chemistry)*, 12, 625 (1963), reacting the addition product with a sultone such as propane sultone or butane sultone or chlorosulphonic acid in a conventional manner to give a sulphonic acid derivative thereof, and then neutralizing the product with an alkali such as a metal hydroxide, e.g., sodium hydroxide, potassium hydroxide or calcium hydroxide or a metal carbonate, e.g., sodium carbonate, ammonia, an amine, e.g., trimethylamine, triethylamine, or triethanolamine. It is generally believed that those compounds have the structures as shown in the specific illustrations of the compounds of this invention but there is a possibility that they include compounds having other structures which can be supposed from the synthesis. However, the inclusion of such materials does not provide any difficulty in the practice of this invention.

The compounds which can be used in this invention are readily soluble in solvents such as water and an organic solvent such as alcohols, e.g., methanol, ethanol, ketones, e.g., acetone or esters, e.g., ethyl acetate. These solvents can be used alone or in combination and when they are incorporated into photographic emulsions, they do not adversely influence the photographic properties of the emulsions such as sensitivity, gamma and fog.

The antistatic polymer used in this invention can be used individually or together with other conventional antistatic agents and the amount of the polymer generally used is about 0.005 to 2.0g, preferably 0.01 to 0.4g, per square metre of photographic film. The content of the polymer is dependent upon the kind of photographic film base used, the kind of photographic composition, the structure of the layers of the photographic material and the coating system.

The antistatic compound can be applied to the surface of a photographic film by dissolving the compound in water and/or an organic solvent, such as an alcohol, e.g., methanol or ethanol, a ketone, e.g., acetone or an ester, e.g., ethyl acetate, used alone or in a mixture. The solution is then applied to the surface of the photographic emulsion layer of the photographic film by spraying or coating on a support, or a photographic film is immersed in the solution, followed by drying. Also, the compound can be used together with a binder such as gelatin, a gelatin derivative such as acylated gelatin as described in U.S. Patents Nos. 2,523,753, 2,691,582 and 3,118,776 or graft gelatin as described in U.S. Patents Nos. 2,831,767 and 3,620,751, polyvinyl alcohol, cellulose

acetate phthalate, cellulose acetate, polyvinyl pyrrolidone, a copolymer of styrene and maleic anhydride or another synthetic polymer. A suitable amount of the polymer is from about 1 to 20 wt. % of the binder, preferably 2 to 10 wt. % of the binder.

The antistatic polymer can be applied as an antistatic treatment to films of cellulose ester, polyester, polystyrene, polycarbonate, polyethylene, polypropylene or other vinylic polymers.

Furthermore, the antistatic layer containing the polymer used in this invention can contain various other additives, such as a hardening agent as disclosed in U.S. Patents Nos. 2,586,168, 2,725,294—5, 2,732,316, 2,983,611, 3,017,280, 3,103,437, 3,186,848, 3,232,763—4, 3,288,775, 3,321,313, 3,325,287, 3,490,911, 3,543,292, 3,635,718 and 3,671,256, a lubricant as disclosed in U.S. Patents Nos. 2,588,765, 2,960,404 and 3,121,060 and British Patent No. 955,061, a matting agent such as titanium dioxide, zinc oxide, silica, polymeric beads as described in U.S. Patents Nos. 2,701,245, 2,992,101 and 3,353,958 or an antihalation dye as disclosed in U.S. Patent No. 3,615,546.

By means of the present invention, the difficulties caused by the formation of static marks occurring as aforesaid during the manufacture or use of photographic materials can be eliminated, even under low humidity conditions; further the antistatic effect thus provided by the polymer is not degraded when the photographic film is stored for a long period of time. Also, the aforesaid difficulties due to excessive surface slippage, such as the slipping of film on cutting of a stack of photographic films and the unwinding of the photographic film in a camera, do not occur. Moreover, when the surface of the emulsion layer of a photographic film of the invention is brought into contact with the back surface of the film under high temperature and high humidity conditions, no adhesion occurs between the two surfaces of the film.

It is particularly surprising that by merely applying the antistatic polymer to the surface of the photographic emulsion side of a photographic material, the surface resistivity of the photographic material is greatly reduced; by contrast, when various conventionally used surface-active agents or known anti-static agents such as saponin, fatty acid esters of sucrose, and the compounds disclosed in the specifications of U.S. Patents Nos. 2,982,651, 3,253,922 and 3,220,847 are applied in this way they have little effect on the surface resistivity.

Also, when the polymer is incorporated in the backing layer of a photographic film it reduces the surface resistivity of the photographic film and provides a backing layer having a surface with an appropriate coefficient of friction and which can readily be mechanically handled. Furthermore, when the antistatic polymer is used together with a conventional antistatic agent which has, as aforementioned, an excellent antistatic property but an undesirably high slipping property, the coefficient of friction of the photographic material can be appropriately increased and its mechanical workability therefore improved without degrading the antistatic property of the photographic material; therefore, such a conventional antistatic agent can be satisfactorily included in photographic materials of the present invention.

The photographic material of the invention can be imagewise exposed to light or X-rays and developed, in conventional manner.

The invention is illustrated by the following Examples, in which parts and percentages are by weight unless otherwise specified, and in which the antistatic property was evaluated by measuring the amount of static charge, the surface resistivity, and the formation of static marks.

The amount of static charge was measured by rolling a sample piece having a width of 1 cm. and a length of 15 cm. with a rubber roller using a load of 380g and a speed of 33 cm/sec and letting it fall in a Faraday cage. The roller used was made of rubber because rubber is positioned in the middle of materials such as plastics, metals, papers and cotton, in the electrostatic charging series and hence rubber is considered to be typical of such materials.

The surface resistivity was determined by inserting the test sample between brass electrodes having a length of 10 cm at an interval of 0.14 cm (stainless steel was used at the portions which contacted the sample) and measuring the one-minute value by means of an insulating resistance tester (MM—V—M type, made by Takeda Riken Co., Ltd.).

The formation of static marks was measured in the following manner. An unexposed photographic film sample was placed on a (white) rubber sheet with the back surface facing the sheet and after pressing the film using a rubber roller from the film side, the sample film was separated from the rubber sheet so as to permit the formation of static marks. The sample was developed for 4 minutes at 20°C in a developer having the following composition:

	water (at 50°C)	700 ml	
	Sodium N-methyl- <i>p</i> -aminophenol sulphate	4 g	
	anhydrous sodium sulphate	60 g	
	hydroquinone	10 g	
5	sodium carbonate monohydrate	53 g	
	potassium bromide	25 g	5
	water to make	1 litre	

fixed in a solution of hypo, and then the formation of static marks on the photographic film was observed and evaluated on a scale of A (no static marks)—B (slight)—C (considerable)—D (extensive)—E (covering entire surface).

#### EXAMPLE 1

To one surface of three samples of a polyethylene terephthalate film was applied an antistatic coating solution prepared as described below, and then a photographic emulsion for a direct X-ray film, containing 9% gelatin and 9% silver halide (AgBrI, iodide content 2 mole %), was applied to the other surface of the film.

##### Antistatic Composition (I):

1% methanol solution of Compound 1 as antistatic agent.

##### Binder Composition (II):

0.3% solution of cellulose triacetate in a mixed solvent consisting of methanol, tetrachloroethylene, tetrachloroethane and phenol in a ratio of 8:70:8:2.

The antistatic coating solutions used were prepared by adding an amount of Antistatic Composition I to 93 grams of Binder Composition II so that the content of the effective component of the antistatic component became, in samples (b) to (d), 2, 3 or 5% of the triacetate binder, and then adding to the mixture further methanol to make a total weight of 12 grams methanol together with that present in Composition I. A control sample (a) was prepared which did not contain any of the Compound 1.

The amount of static charge, the surface resistivity, and the amount of static marks formed of these sample films after processing were measured under the conditions of 23°C and RH of 65% and the results are shown as follows:

TABLE 1

Sample	Amount of Compound 1 (wt. % of binder)	Static Charges (volts)	Surface Resistivity (ohms)	Static Marks (grade)
(a)	0	50	$>10^{16}$	E
(b)	2	40	$7 \times 10^{10}$	A—B
(c)	3	23	$6 \times 10^{10}$	A
(d)	5	10	$3 \times 10^9$	A

It is clear from the above results that the amount of static charges and the surface resistivity were markedly less in the samples (b) to (d) according to this invention as compared with the control sample. Also, in samples (b) to (d), no or almost no formation of static marks was observed.

#### EXAMPLE 2

To one surface of two samples of a polyethylene terephthalate film there was applied the following Binder Composition III which was then dried for 10 minutes at 120°C.

##### Binder Composition (III):

	cellulose triacetate	0.3 g	
	methanol	10 g	
	ethylene chloride	70 g	
	methylene dichloride	15 g	
	tetrachloroethane	5 g	

Then, an Antistatic Composition IV having the following composition was applied to the binder layer of one sample (b) of the film and dried for 10 minutes at 120°C.

Antistatic Composition (IV):  
Compound 3  
methanol

0.2 g  
100 g

Thereafter, a photographic emulsion for an indirect X-ray film, containing 9% gelatin and 9% silver halide (AgBrI, iodide content 3 mole %), was applied to the other surface of both the film samples (a) and (b) and dried. The photographic film thus prepared was humidified for 3 hours at 23°C and a RH of 60% and then the surface resistivity and the formation of static marks were measured, the results being shown in the following table.

TABLE 2

Sample	Surface Resistivity (ohms)	Static Marks
(a) control	$>10^{16}$	D
(b) with layer of Antistatic Composition IV	$3.5 \times 10^8$	A

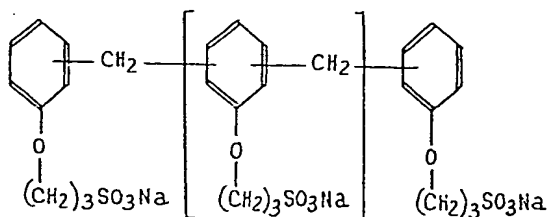
As is clear from the results in Table 2, in the film sample (a) having only the layer of the Binder Composition, the surface resistivity was not reduced and the formation of static marks was severe. On the other hand, in the sample (b) also having the layer of Antistatic Composition containing the Compound 3, the surface resistivity was reduced greatly, no formation of static marks was observed, and thus a satisfactory antistatic effect was obtained.

## EXAMPLE 3

Three samples of cellulose triacetate film base were each coated on one surface with a layer of solution of cellulose diacetate of the following composition and dried for 10 minutes at 80°C.

cellulose diacetate	0.2 g
water	10 g
methanol	50 g
acetone	40 g
Compound 3 or 9	0.1 g

The coating solution used for sample (a) was a control and contained no antistatic agent; for sample (b) of the invention it contained Compound 3, and for sample (x) it contained a comparative Compound 9 of the following structural formula and mean polymerization degree=5.



A photographic emulsion containing 9% gelatin and 9% silver halide (AgBrI, iodide content 2 mole %) was applied to the opposite surface of each film sample and dried. After humidifying the back surface of each photographic film for 3 hours at 23°C and a RH of 60%, the surface resistivity and the formation of static marks were measured, the results being shown as follows:

TABLE 3

Sample	Antistatic agent in layer on back	Surface Resistivity (ohms)	Static Marks
(a)	Control—none	$10^{16}$	D
(x)	Comparison—Compound 9 w/o alkyl group	$5 \times 10^{12}$	C
(b)	As invention—Compound 8	$1.3 \times 10^9$	A



As is clear from these results, in the control sample (a) the surface resistivity was not reduced and the formation of static marks was severe: the comparative compound 9 which did not contain an alkyl phenol group gave but a poor improvement. In the sample (b) according to this invention, the surface resistivity was reduced greatly, no static marks were observed, and thus a satisfactory antistatic effect was obtained.

#### EXAMPLE 4

A radiographic material was prepared by applying a highly sensitive photographic emulsion for an X-ray film containing 6% gelatin and 6% silver iodobromide (iodide content 3 mole %) to subbed acetyl cellulose film, covering the emulsion layer with a simple aqueous solution of gelatin (not containing an antistatic agent) as a surface protective layer and drying. Seven samples were taken from this material and except for a control sample (a), they were each immersed for 30 seconds in a 1% aqueous solution of a compound used in this invention, namely the Compounds 1, 3, 4 and 7, or of the known antistatic agent saponin or sucrose monolauric acid ester, and then dried.

After humidifying each of the samples thus prepared at 23°C and an RH of 40%, the amount of static charge and the surface resistivity of the sample were measured under these conditions, the results of which are shown as follows.

TABLE 4

Sample	Antistatic Agent	Static Charge (volts)	Surface Resistivity (ohms)	Static Marks
(a)	Untreated	28	$10^{12.5}$	E
(x)	Saponin	15	$10^{12}$	D
(y)	Sucrose monolauric acid ester	13	$10^{12}$	D
(b)	Compound 1	2	$10^{11}$	A
(c)	" 3	1	$10^{11}$	A
(d)	" 4	4	$10^{10.5}$	A
(e)	" 7	8	$10^{11}$	B

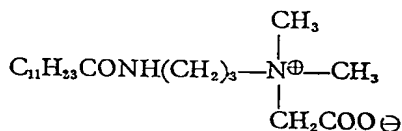
As is clear from the results contained in Table 4, in the photographic films (samples (b) to (e)) impregnated with a compound used in this invention, no or almost no formation of static marks was observed and they showed an extremely reduced surface resistivity.

On the other hand, in the comparison samples (x) and (y) impregnated with a known antistatic agent, static marks formed severely and almost no reduction in resistivity was observed. Furthermore, in the control untreated sample (a), stain-like static marks formed on the entire surface of the film.

#### EXAMPLE 5

This example illustrates the conjoint use of a known surfactant and of an antistatic polymer.

Samples of the radiographic material (containing no antistatic agent) used in Example 4 were immersed for 30 seconds in an aqueous solution of Compound 1 alone or admixed with an amphoteric surface-active agent having the following formula:



and each sample was then dried and tested as in Example 4, the results of which are shown as follows:

Sample	Antistatic Agent	Static Charge (volts)	Surface Resistivity (ohms)	Static Marks
(a)	Untreated	28	$10^{12.5}$	E
(b)	Compound 1 (1%)	5	$10^{10}$	A
(c)	Compound 1 (0.5%) and Amphoteric Surface-Active Agent (0.25%)	1	$10^9$	A

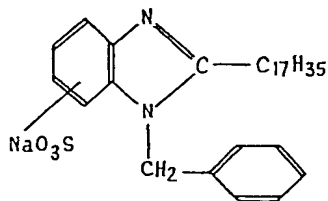
As is clear from these results, the sample (c) impregnated with both the polymer used in this invention and the amphoteric surface-active agent showed a lower surface resistivity than that of the sample (b) treated only with the polymer used in this invention. Also, no static marks were observed with sample (a) or (b) in this Example.

#### EXAMPLE 6

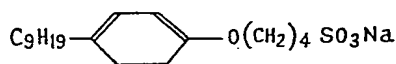
That the polymer used in this invention has an anti-slip property (in addition to an antistatic property) was demonstrated by comparing its effect on the coefficient of dynamic friction with that of known antistatic agents.

Example 1 was repeated but using as the antistatic agent in Composition (I) the following compounds:

Compound 1 used in this invention  
Known Antistatic Agent A



Known Antistatic Agent B



in the concentrations shown in the table below.

The antistatic coating solutions used above were prepared by adding Antistatic Composition I to Binder Composition II so that the content of the effective agent became 3.4% by weight of the binder and then adding the further methanol.

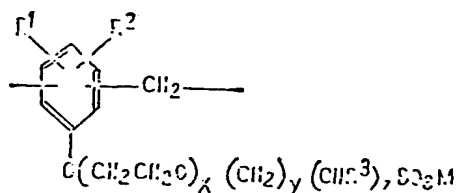
The coefficient of dynamic friction was measured as follows. The sample was placed on a movable base, a 20 g steel ball of a diameter of 5 mm was placed on the sample and then the coefficient of dynamic friction was determined from the force applied to the steel ball when the base was moved at a speed of 0.6 cm/sec. The temperature and humidity conditions for the measurement were 23°C and a relative humidity of 65%. The results obtained are shown in the following table.

Antistatic Agent	Amount of agent (wt. % of binder)	Coefficient of Dynamic Friction
(a) None (control)	0	0.26
(b) Compound 1	4	0.26
(c) Antistatic Agent A and Compound 1	4	0.21
(d) Antistatic Agent A and Compound 1	1	0.25
(e) Antistatic Agent B and Compound 1	4	0.23
(f) Antistatic Agent B and Compound 1	1	0.25
(x) Antistatic Agent A	4	0.17
(y) Antistatic Agent B	4	0.20

As is clear from the results shown above, the coefficients of dynamic friction obtained by using the polymers used in this invention are larger than those obtained by using known antistatic agents alone. Moreover, by using the polymers together with another antistatic agent, the coefficient of dynamic friction can be increased.

#### WHAT WE CLAIM IS:—

1. A photographic material comprising a support having thereon at least one silver halide light-sensitive emulsion layer and at least one other layer, said photographic material containing in at least one layer as an antistatic agent, a polymer consisting essentially of recurring units represented by the general formula:



wherein R<sup>1</sup> represents a hydrogen atom or an alkyl group, R<sup>2</sup> represents an alkyl group, R<sup>3</sup> represents a hydrogen atom or a methyl group, M represents a hydrogen atom or a cation, x has a value of from 0 to 50, y represents 0, 2 or 3, and z represents 0 or 1, provided that x, y and z are not all simultaneously zero.

2. A photographic material as claimed in Claim 1, in which said polymer has a mean polymerization degree of 2 to 20.

3. A photographic material as claimed in Claim 2, in which the polymerisation degree is 2 to 10.

4. A photographic material as claimed in Claim 1, 2 or 3, in which the or each alkyl group contains 1 to 18 carbon atoms.

5. A photographic material as claimed in any of Claims 1 to 4, in which x has a value of from 1 to 50.

6. A photographic material as claimed in Claim 1, in which said polymer is any of the Compounds 1 to 8 described hereinbefore.

7. A photographic material as claimed in any preceding claim, in which said polymer is present in an amount of 0.005 to 2.0 grams per square metre of the surface area of said photographic material.

8. A photographic material as claimed in any of Claims 1 to 7, in which said polymer is present in a silver halide emulsion layer of said photographic material.

9. A photographic material as claimed in any of Claims 1 to 7, in which said polymer is present in a surface protective layer of said photographic material.

10. A photographic material as claimed in any of Claims 1 to 7, in which said polymer is present in the backing layer of said photographic material.

11. A photographic material as claimed in any of Claims 1 to 7, in which said polymer is present in a layer on the surface of a photographic emulsion layer of said photographic material.

12. A photographic material as claimed in any of Claims 1 to 7, in which said polymer is present in a layer on the back surface of said support of said photographic material.

13. A photographic material as claimed in any preceding claim, wherein the anti-static polymer is present in a layer comprising a binder.

14. A photographic material as claimed in Claim 10, wherein the binder is gelatin, a cellulose derivative or a synthetic polymer or copolymer.

15. A photographic material as claimed in any preceding claim, wherein another antistatic compound is also present in the material.

16. A photographic light-sensitive material substantially as hereinbefore described with reference to any one of the foregoing Examples 1 to 6 apart from Comparative sample (a), (x) or (y).

17. A method of making a photographic material as claimed in any of Claims 1 to 7 which includes the step of coating a solution of the polymer used as the antistatic agent on the emulsion side or the back side of the material.

18. A method as claimed in Claim 17, wherein the coating solution also includes a binder.

19. A method of making a photographic material as claimed in any of Claims 1 to 15 which comprises immersing a photographic light-sensitive material in a solution of the polymer.

20. Photographic material prepared by a method as claimed in any of Claims 17 to 19.
21. Photographs or radiographs obtained by imagewise exposing and developing a photographic material as claimed in any of Claims 1 to 16 or 20.

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